Supporting Information
for

Kinetics and Products of the Acid-Catalyzed Ring Opening of Atmospherically Relevant Butyl Epoxy Alcohols

Nathan C. Eddingsaas,[*,†] David G. VanderVelde,[†] and Paul O. Wennberg[‡,‖]

Divisions of Chemistry and Chemical Engineering, Geological and Planetary Sciences, and Engineering and Applied Science, California Institute of Technology, MC 127-72, 1200 East California Boulevard, Pasadena, California 91125

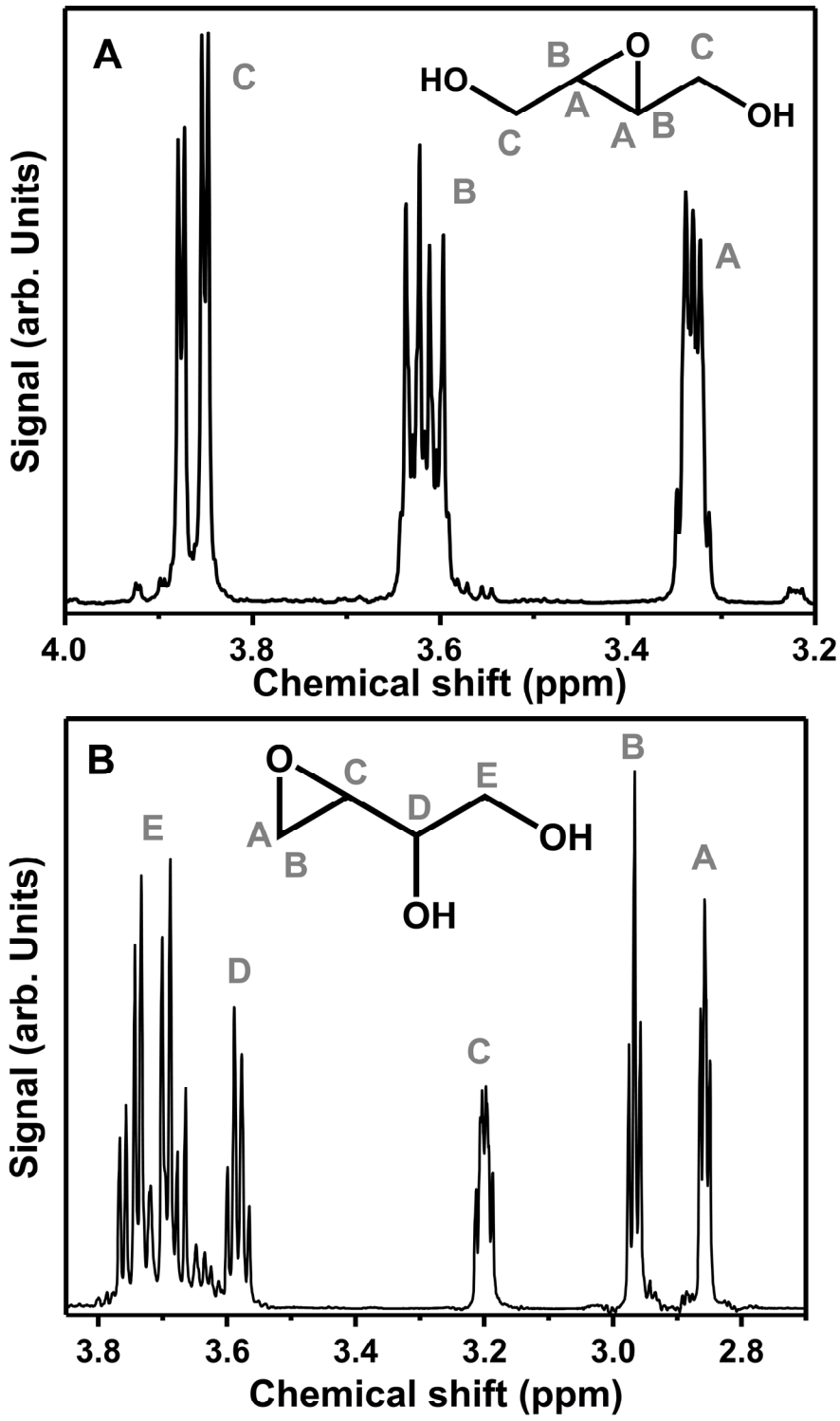

Figure S1. ^{1}H NMRs of synthesized hydroxy substituted epoxides, (A) 2,3-epoxybutane-1,4-diol, (B) 34-epoxybutane-1,2-diol, (C) 2-methyl-2,3-epoxybutan-1-ol, (D) 2-methyl-3,4-epoxybutn-1-ol, unmarked peaks are from 2-methyl-1,2,4-butantriol. In all ^{1}H NMR spectra, the chemical shift of D_2O was set to 4.79 ppm.

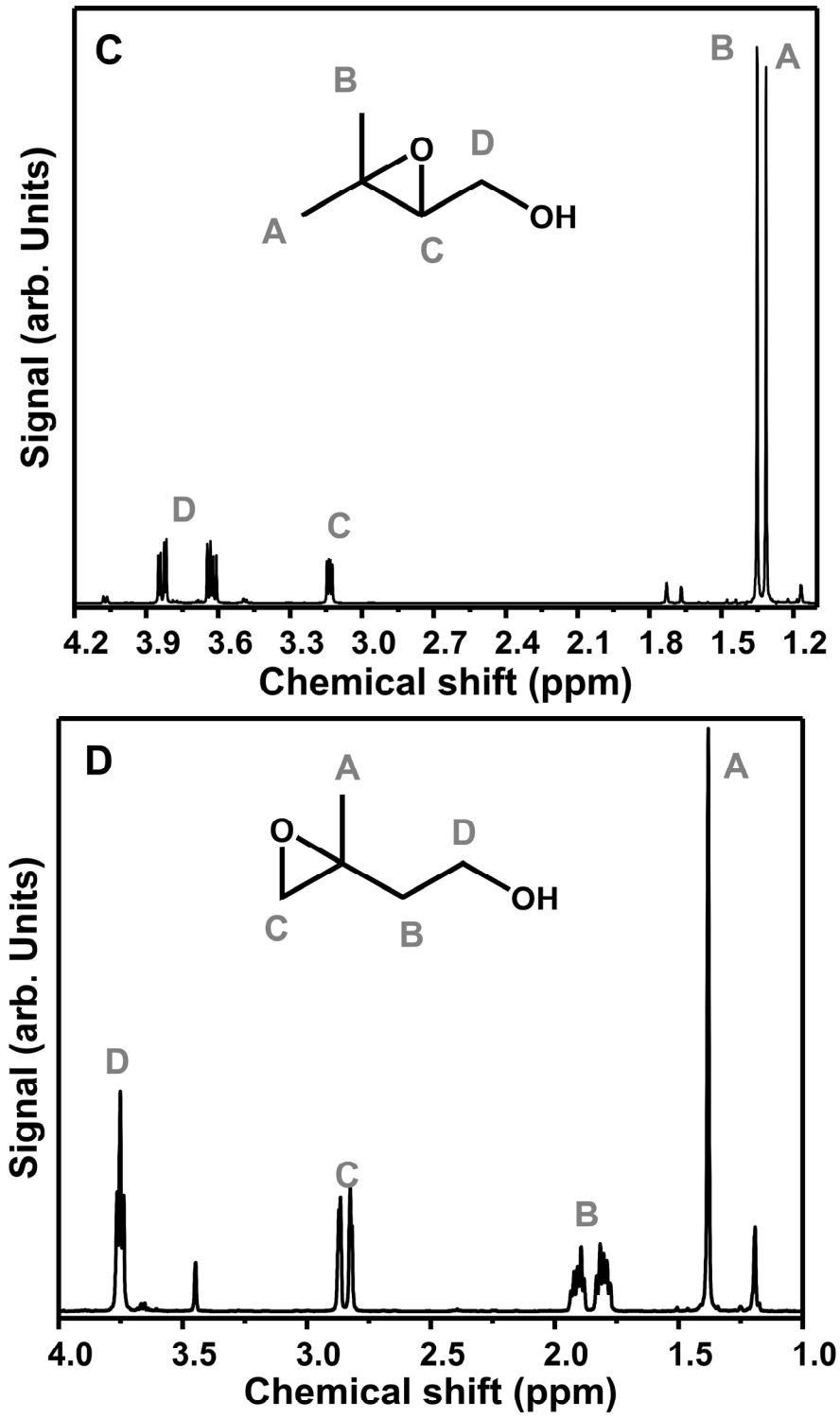

Figure S1 continued.

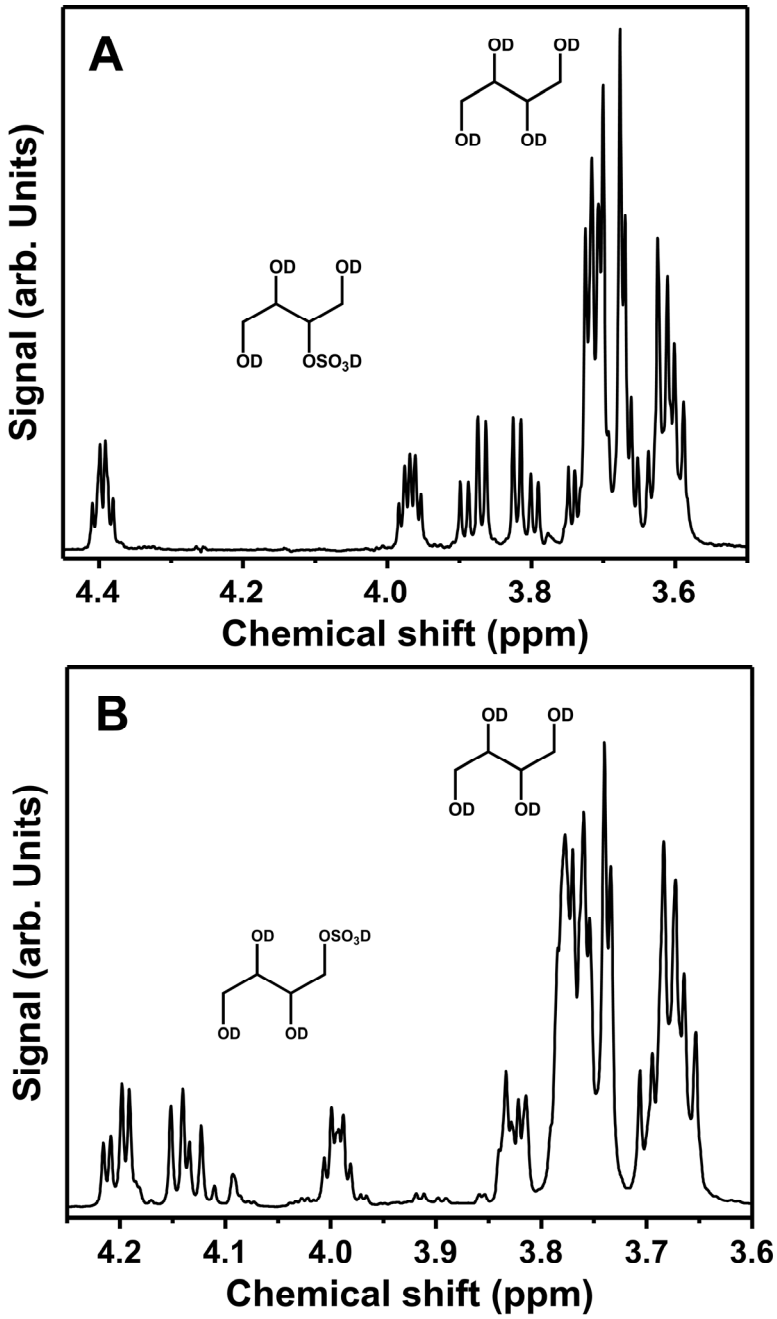

Figure S2. ^{1}H NMRs of the products of epoxides in 0.1 M D_2SO_4 and 1.0 M Na_2SO_4, (A) 2,3-epoxybutane-1,4-diol, (B) 34-epoxybutane-1,2-diol, (C) 2-methyl-2,3-epoxybutan-1-ol, stared peak is from the CH_3 groups of 2-methyl-3,4-hydroxybutane-2-sulfate.

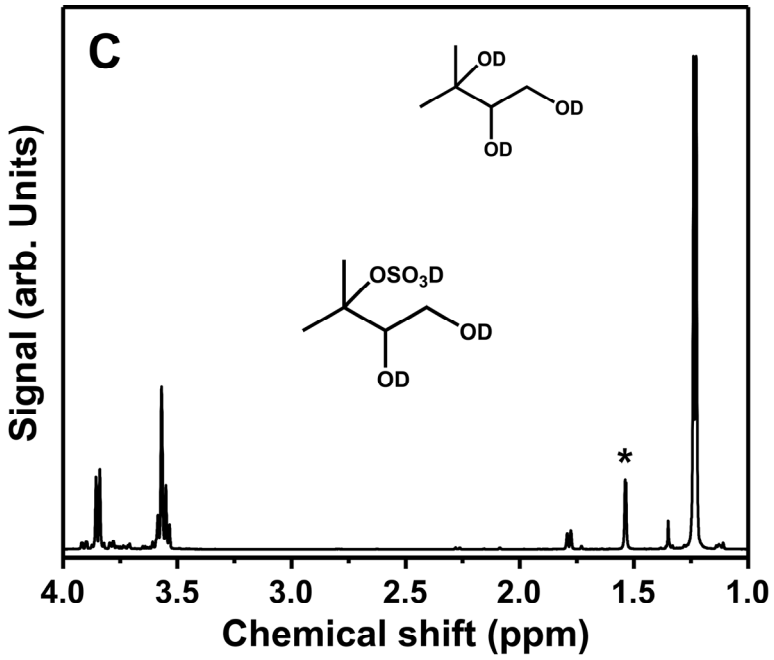

Figure S2 continued.

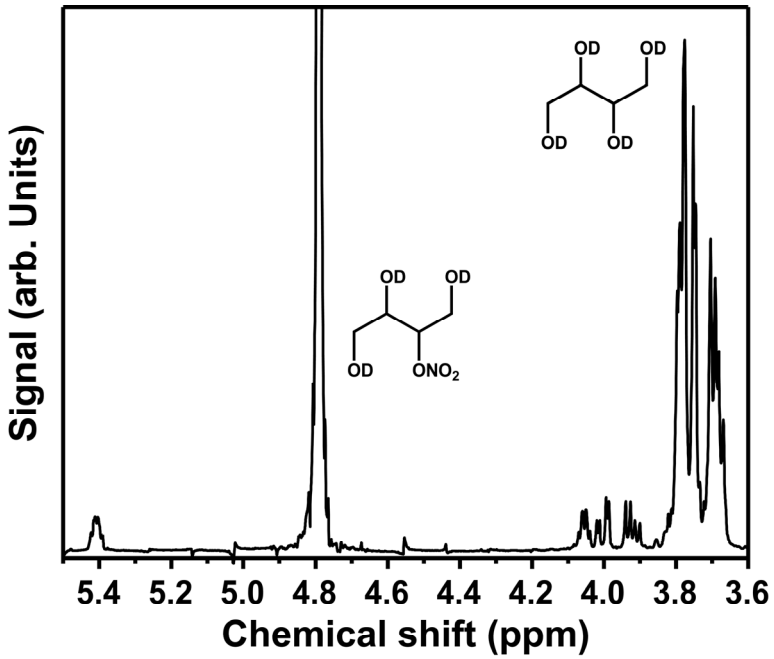

Figure S3. ^{1}H NMR of 2,3-epoxybutane-1,4-diol in 0.1 M HNO_3, 1.0 M $NaNO_3$.

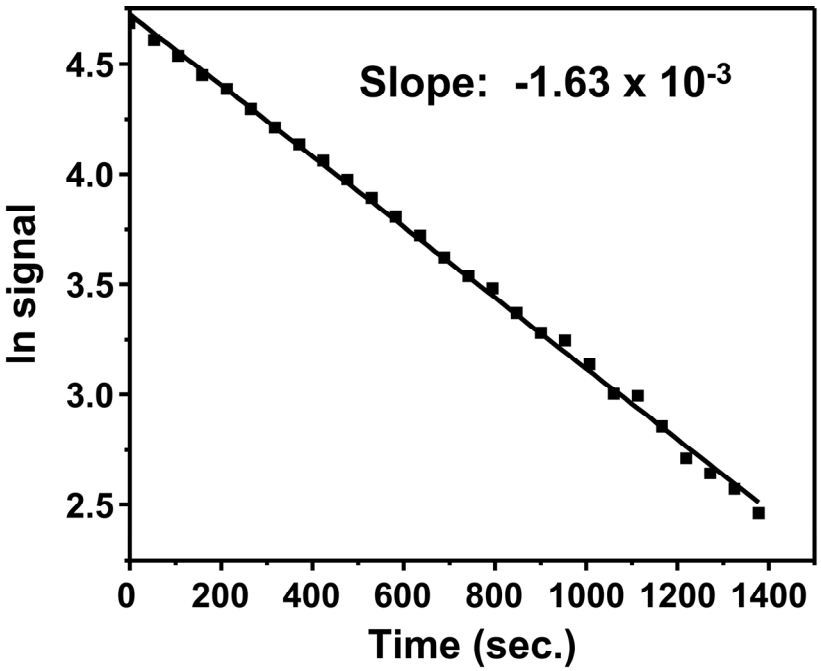

Figure S4. Kinetic analysis of the ring opening of 3,4-epoxybutane-1,2-diol in 0.5 M D_2SO_4. ln of integrated area of ^1H NMR peak of the epoxide at 2.85 ppm as a function of reaction time of acid-catalyzed ring opening along with the best linear fit to the data shows first order kinetics. Greater than 90% of the epoxide reacted over the course of the kinetic run.

Model of atmospheric loss of isoprene epoxydiols:

Key:
$IEPOX_g$: Gas phase isoprene epoxydiol
$IEPOX_{ox}$: Gas phase oxidation products of isoprene epoxydiol
$IEPOX_{dd}$: Dry deposition of isoprene epxoydiol
$IEPOX_a$: Aerosol phase isoprene epoxydiols
$IEPOX_{rop}$: Condensed phase ring-opening products of isoprene epoxydiols
k_{ox}: Gas phase oxidation rate constant
k_{dd}: Dry deposition rate constant
k_{par}: Rate constant for aerosol partitioning
k_{vol}: Rate constant for vaporization back to gas phase
k_{H^+}: Acid-catalyzed epoxide ring-opening rate constant

Rate equations:

The model of the loss processes of isoprene epoxydiols consists of four equations (1-4).

$$IEPOX_g + OH \xrightarrow{k_{ox}} IEPOX_{ox} \quad (1)$$

$$IEPOX_g \xrightarrow{k_{dd}} IEPOX_{dd} \quad (2)$$

$$IEPOX_g \underset{k_{vol}}{\overset{k_{par}}{\rightleftharpoons}} IEPOX_a \quad (3)$$

$$IEPOX_a + H^+ \xrightarrow{k_{H^+}} IEPOX_{rop} \quad (4)$$

The model results in the following concentration expressions:

$$\frac{d\left[IEPOX_g\right]}{dt} = -k_{ox}\left[IEPOX_g\right] - k_{dd}\left[IEPOX_g\right] - k_{dep}\left[IEPOX_g\right] + k_{vol}\left[IEPOX_a\right] \quad (5)$$

$$\frac{d\left[IEPOX_a\right]}{dt} = k_{dep}\left[IEPOX_g\right] - k_{vol}\left[IEPOX_a\right] - k_{H^+}\left[IEPOX_a\right] \quad (6)$$

$$\frac{d\left[IEPOX_{rop}\right]}{dt} = k_{H^+}\left[IEPOX_a\right] \quad (7)$$

The rate constants for k_{ox}, k_{dd}, and k_{H^+} are derived from:

$$k_{ox} = 5.78\times10^{-11}\cdot e^{-400/T}\cdot\left[OH\right] \quad (8)$$

$$k_{dd} = dv/blh \quad (9)$$

where *dv* is deposition velocity and *blh* is boundary layer height

$$k_{H^+} = 5\times10^{-2}\cdot\left[H^+\right] \quad (10)$$

where $[H^+]$ is determined from the pH of the aerosol. The values used for each of the variables can be found in the main text is section 4.

The partitioning between $IEPOX_g$ and $IEPOX_a$ is represented by an equilibrium rate equation with fast equilibrium kinetics. The equilibrium constant (k_{eq}) varies with the liquid water content. At 10 μg m^{-3} k_{eq} = 3 x 10^{-2} sec^{-1} where k_{par} was set to 1.0 x 10^{-3} sec^{-1} resulting in k_{vol} = 3.3 x 10^{-2} sec^{-1}. At 100 μg m^{-3} k_{eq} = 0.25 sec^{-1} where k_{par} was set to 1.0 x 10^{-3} sec^{-1} resulting in k_{vol} = 4.0 x 10^{-3} sec^{-1}. The rate of the forward (partitioning) and reverse (volatilization) insured that equilibrium was reached rapidly and was allowed to stay at

equilibrium while $IEOPX_g$ was lost to oxidation and dry deposition and $IEPOX_a$ was lost to acid-catalyzed ring opening.

A kinetic model was constructed consisting of the major reaction channels for isoprene epoxydiols. We use the kinetics simulation software Kintecus[1] following the decay of gas-phase epoxydiols for 20 hours to insure completion of the reactions. The inputs to the model were varied to observe how the aerosol properties influence the aerosol yield from isoprene epoxydiols (Fig. S1). The rates of gas-phase oxidation and deposition were held constant while the LWC and pH of the aerosol was varied to influences the gas to particle partitioning and rate of liquid-phase epoxide ring-opening respectively. See Table S1 for a tabular representation of the results. Both pH and LWC of the aerosol influence the yield of aerosol-phase ring opening of isoprene epoxydiols with low pH and high LWC favoring this process.

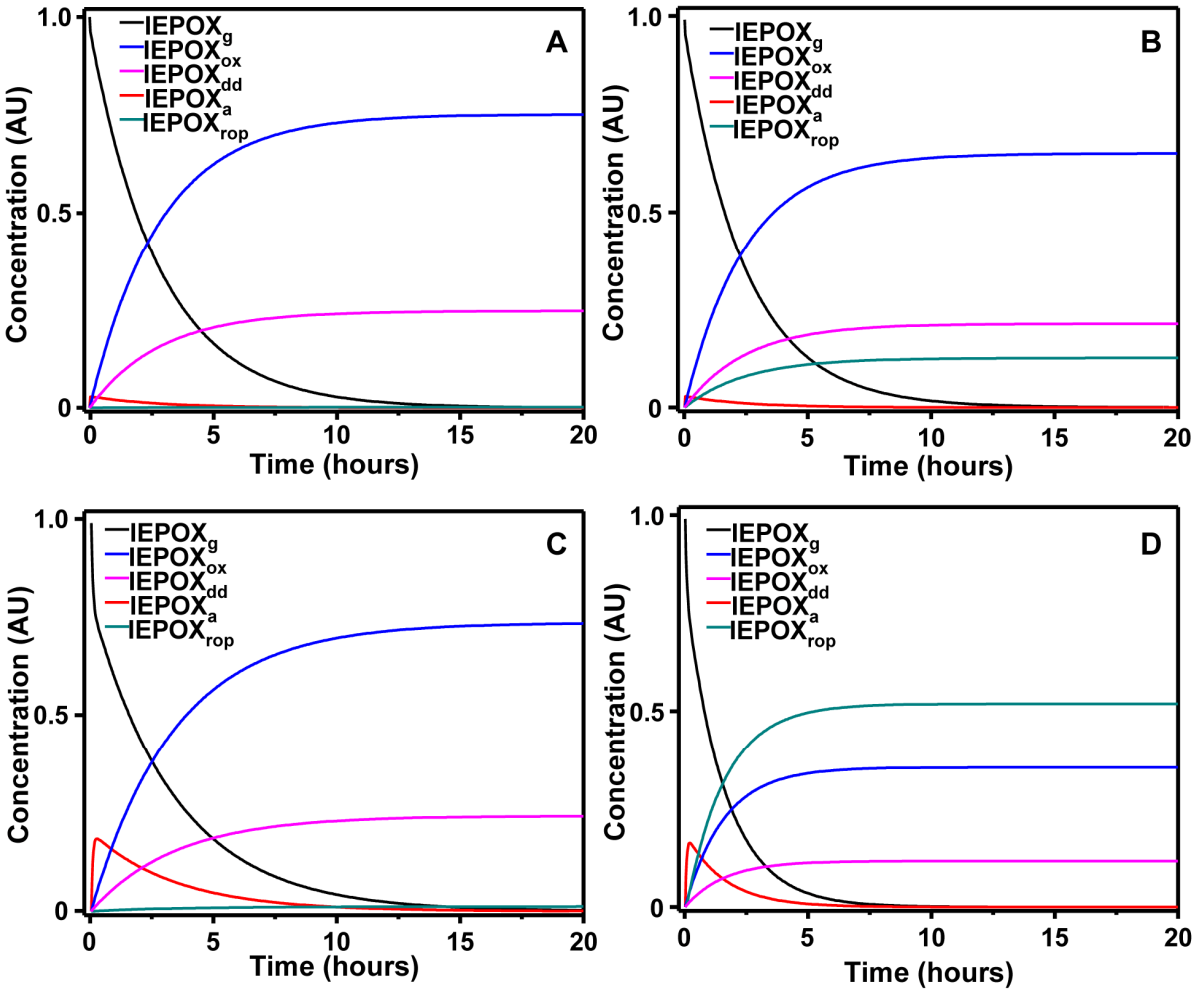

Figure S5: Kinetic simulation of loss of isoprene epoxydiols upon varying the liquid water content (LWC) and pH of the aerosol, (A) LWC = 10 μg m^{-3}, pH = 4, (B) LWC = 10 μg m^{-3}, pH = 2, (C) LWC = 100 μg m^{-3}, pH = 4, (D) LWC = 100 μg m^{-3}, pH = 2. In all cases the rate of gas-phase oxidation and dry-deposition are held constant. The percent of each component after 20 hours can be seen in Table S1, a reprint of Table 3 from the main text.

Table S1. Summary of the atmospheric fate of isoprene epoxydiols after 20 hours as determined by the kinetic model described within the text.

aerosol properties	aerosol phase reaction products	gas phase oxidation[a]	dry deposition[b]
LWC: 10 μg m^{-3}, pH: 4	0.2%	75%	25%
LWC: 10 μg m^{-3}, pH: 2	13%	66%	21%
LWC: 100 μg m^{-3}, pH: 4	1.3%	74%	24%
LWC: 100 μg m^{-3}, pH: 2	52%	36%	12%

a. $k_{ox} = 7.6 \times 10^{-5}$ s^{-1}
b. $k_{dd} = 2.5 \times 10^{-5}$ s^{-1}

References:

(1) Ianni, J. C., **Kintecus**, Window v. 2.80, 2002, www.kintecus.com